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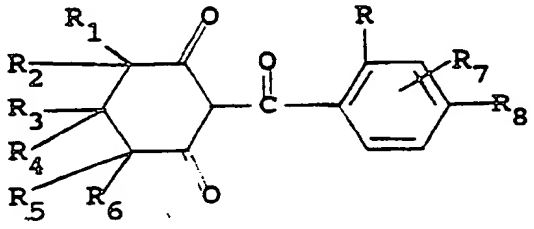

(I)

(57) Abstract

A herbicidal composition comprising herbicidally effective amounts of a substituted cyclohexanedione of formula (I) in which: R is halogen; C_1-C_2 alkyl, preferably methyl; C_1-C_2 alkoxy, preferably methoxy; nitro; cyano; C_1-C_2 haloalkyl, preferably trifluoromethyl; or R^aSO_n- wherein n is 0 or 2, preferably 2 and R^a is C_1-C_2 alkyl, preferably methyl. Preferably, R is chlorine, bromine, C_1-C_2 alkyl, C_1-C_2 alkoxy, cyano, nitro, C_1-C_2 alkylthio or C_1-C_2 alkylsulfonyl; more preferably chlorine, nitro, methyl, trifluoromethyl or methylsulfonyl; R_1, R_2, R_3, R_4, R_5 and R_6 and independently hydrogen; C_1-C_4 alkyl, preferably C_1-C_2 alkyl, more preferably methyl or hydrogen; R_7 and R_8 are independently (1) hydrogen; (2) halogen, preferably chlorine, fluorine or bromine; (3) C_1-C_4 alkyl, preferably methyl; (4) C_1-C_4 alkoxy; preferably methoxy or ethoxy; (5) trifluoromethoxy; (6) cyano; (7) nitro; (8) C_1-C_4 haloalkyl, more preferably trifluoromethyl; (9) R^bSO_n- wherein n is the integer 0, 1 or 2, preferably 0 or 2; and R^b is (a) C_1-C_4 alkyl, preferably methyl; or (b) C_1-C_4 alkyl substituted with halogen, preferably chloromethyl, or trifluoromethyl; (10)-NR^cR^d wherein R^c and R^d are independently hydrogen or C_1-C_4 alkyl; (11) $R^eC(O)$ - wherein R^e is C_1-C_4 alkyl or C_1-C_4 alkoxy; (12) -$SO_2NR^cR^d$ wherein R^c and R^d are as defined; (13) -$N(R^c)C(O)R^d$ wherein R^c and R^d are as defined; and (14) -$CH_2CH_2OCH_3$ or -$CH_2CH_2OC_2H_5$; at least one nitrogen containing fertilizer that is present in an amount that increases the herbicidal activity of said substituted cyclohexanedione; and one or more adjuvants.

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herbicidal substituted cyclohexanedione and nitrogen fertiliser compositions and method

Background of the Invention

In many cases, novel mixtures of known agrochemicals have been shown to be more effective in combination than when applied individually. The present invention resides in the discovery of novel herbicidal compositions which comprise herbicidally effective amounts of substituted cyclohexanedione, nitrogen sources and adjuvants. In another embodiment, the composition also includes a substantially non-phytotoxic, antidotally effective amount of a cyclohexanedione herbicide antidote.

The invention also comprises a method of controlling undesirable vegetation in the presence of a crop, particularly a corn crop, by applying to the locus of the crop or undesired vegetation a herbicidal composition comprising herbicidally effective amounts of the cyclohexanedione, the nitrogen source, and one or more adjuvants.

Prior Art

The compounds forming the combination which is the subject of the present invention are independently known in the art for their effects on plant growth. Cyclohexanediones are disclosed as herbicides in U.S. Patent Nos. 4,780,127 (Michaely et al., June 30, 1986); 4,946,981 (Carter et al., August 7, 1990); 4,816,066 (Michaely et al., March 28, 1989); and 4,781,751 (Chin, November 1, 1988). Nitrogen is well known in the art as a fertilizer and is described in the Farm Chemicals Handbook, 1988 Edition on pages B48 and B49. Commercially available nitrogen fertilizers include anhydrous ammonia, ammonium nitrate, ammonium sulfate, urea, nitrogen solutions (which include urea ammonium nitrate), ammonium phosphate,

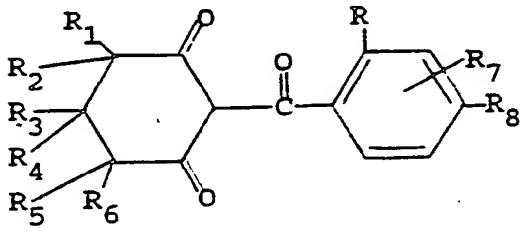
potassium nitrate, and combinations thereof. Other fertilizers include methyl ammonia, ammonia chloride and methyl ammonia chloride. Other compounds used in the herbicidal composition of this invention are adjuvants. The term adjuvant includes materials such as wetting agents, spreaders, emulsifiers, dispersing agents, surfactants and the like.

Additionally, synergistic compositions employing cyclohexanediones and other herbicides are disclosed in U.S. Patent No. 4,759,794 (Hsu, July 26, 1988). This patent specifically claims the cyclohexandione 2-(2-chloro-4-methanesulfonylbenzoyl)-1,3-cyclohexandione in combination with specific benzoic acid, (3-amino-2,5 dichlorobenzoic acid); acetanilide (2-chloro-N-isopropylacetanile); and triazine (2-chloro-4-(ethylamino)-6-isopropylamino)s-triazine) herbicides.

Description of the Invention

It has been discovered that the control of undesirable vegetation is exhibited by compositions comprising a mixture of the following compounds:

a) an herbicidally effective amount of a substituted cyclohexanedione of the formula



in which

R is halogen; C_1-C_2 alkyl, preferably methyl; C_1-C_2 alkoxy, preferably methoxy; nitro; cyano; C_1-C_2 haloalkyl, preferably trifluoromethyl; or R^aSO_n- wherein n is 0 or 2, preferably 2 and R^a is C_1-C_2 alkyl, preferably methyl. Preferably, R is chlorine, bromine, C_1-C_2 alkyl, C_1-C_2 alkoxy, cyano, nitro, C_1-C_2 alkylthio or C_1-C_2 alkylsulfonyl; more preferably chlorine, nitro, methyl, trifluoromethyl or methyl-

sulfonyl;

R_1, R_2, R_3, R_4, R_5 and R_6 are independently hydrogen; C_1-C_4 alkyl, preferably C_1-C_2 alkyl, more preferably methyl or hydrogen;

R_7 and R_8 are independently (1) hydrogen; (2) halogen, preferably chlorine, fluorine or bromine; (3) C_1-C_4 alkyl, preferably methyl; (4) C_1-C_4 alkoxy, preferably methoxy or ethoxy; (5) trifluoromethoxy; (6) cyano; (7) nitro; (8) C_1-C_4 haloalkyl, more preferably trifluoromethyl; (9) R^bSO_n- wherein n is the integer 0, 1 or 2, preferably 0 or 2; and R^b is (a) C_1-C_4 alkyl, preferably methyl; or (b) C_1-C_4 alkyl substituted with halogen, preferably chloromethyl, or trifluoromethyl; (10) $-NR^cR^d$ wherein R^c and R^d are independently hydrogen or C_1-C_4 alkyl; (11) $R^eC(O)$- wherein R^e is C_1-C_4 alkyl or C_1-C_4 alkoxy; (12) $-SO_2NR^cR^d$ wherein R^c and R^d are as defined; (13) $-N(R^c)C(O)R^d$ wherein R^c and R^d are as defined; and (14) $-CH_2CH_2OCH_3$ or $-CH_2CH_2OC_2H_5$;

b) at least one nitrogen containing fertilizer that is present in an amount that increases the herbicidal activity of said substituted cyclohexanedione; and

c) one or more adjuvants.

Preferred cyclohexanediones are those in which R is chlorine, bromine, nitro, methyl or trifluoromethyl, most preferably, R is chloro and preferably R^7 is in the 3-position. More preferably, R^7 is hydrogen, C_1-C_3 alkoxy, $-CH_2CH_2OCH_3$, $-CH_2CH_2OC_2H_5$, or C_1-C_4 thioalkyl. More preferably, R^7 is hydrogen, methylthio, methoxy, ethoxy, $-CH_2CH_2OCH_3$ or $-CH_2CH_2OC_2H_5$. Most preferably, R^8 is halogen, trifluoromethyl, or R^bSO_n wherein R^b is C_1-C_4 alkyl, preferably methyl or ethyl, and n is the integer 0 or 2.

The most preferred cyclohexanediones are 2-(2-chloro-3-ethoxy-4-ethylsulfonyl benzoyl)-5-methyl-1,3-cyclohexanedione and 2-(2-chloro-3-ethoxyl-4-ethylsulfonyl benzoyl)-1,3-cyclohexanedione. These compounds are disclosed in U.S. Patent No. 4,780,127 and a key process for their preparation is disclosed

in U.S. Patent No. 4,695,673. These references are hereby incorporated by reference.

The term "C_1-C_4 alkyl" includes methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl and t-butyl. The term "halogen" includes chlorine, bromine, iodine and fluorine. The term "C_1-C_4 alkoxy" includes methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, isobutoxy and t-butoxy. The term "C_1-C_4 haloalkyl" includes the alkyl groups defined above under C_1-C_4 alkyl in which one or more hydrogen is replaced by chloro, bromo, iodo or fluoro.

Nitrogen sources used in fertilizing materials are commonly classified as either nitrate or ammonium types. Commercially available ammonium types include anhydrous ammonia, aquaammonia, ammonium nitrate, ammonium sulfate, fluid nitrogen fertilizers, urea, and ammonium phosphates. The nitrate type fertilizers include ammonium nitrate, nitrogen solutions, calcium nitrate and sodium nitrate. The preferred nitrogen fertilizers are nitrogen solutions. The most preferred nitrogen fertilizer is urea ammonium nitrate (UAN) wherein the % N is about between 28-33%. This solution and other nitrogen solutions within the scope of the present invention can be prepared by known procedures in the art.

The preferred adjuvants include nonionic, anionic, cationic and amphoteric surfactants. Examples of anionic surfactants include:

a) carboxylic acid salts, for example, sodium and potassium salts of coconut oil fatty acids;

b) sulfonic acid salts, for example, linear alkyl benzene sulfonates, sodium, calcium and ammonium lignosulfonates, petroleum sulfonates, paraffin sulfonates, and alkyl naphthalene sulfonates;

c) sulfuric acid ester salts, for example, sulfated linear primary alcohols; and

d) phosphonic and polyphosphonic acid esters, for example, sodium alkyl phosphate (not oxyethylenated).

Examples of cationic surfactants include:

a) long chain amines;

b) quaternary ammonium salts, for example, cetyltrimethyl ammonium bromide and N-alkyl trimethyl ammonia chloride; and

c) polyoxyethylenated long chain amines.

Examples of nonionic surfactants include:

a) polyoxyethylenated alkyl phenols;

b) polyoxyethylenated straight-chain alcohols;

c) polyoxyethylenated polyoxypropylene glycols;

d) glyceryl and polyglyceryl esters of natural fatty acids;

e) propylene glycol, sorbital polyoxyethylenated sorbital esters;

f) alkanolamines;

g) tertiary acetylenic glycols;

h) polyoxyethylenated silicones;

i) N-alkyl pyrrolidones; and

j) alkyl polyglycosides.

Examples of ampholytic surfactants include:

a) β-N-alkylaminopropionic acids;

b) N-alkyl-β-iminodipropionic acids;

c) imidazoline carboxylates;

d) N-alkylbetaines;

e) amino oxides;

f) sulfobetaines or sultaines; and

g) phosphatides.

These surfactants and others are described in Drew Myers, Surfactant Science and Technology, (New York: VCH Publishers, Inc., 1988), Chapter 2 and Milton J. Rosen, Surfactants and Interfacial Phenomena, 2nd Edition, (New York: John Wiley and Sons, Inc., 1989), Chapter 1. These references are hereby incorporated by reference.

Exemplary surfactants found to be useful in the compositions of this invention include the following: polyoxyethylene sorbitan monolaurates, manufactured by ICI Americas Inc. and sold under the tradename Tween 20; alkylaryl-polyoxyethylenes, manufactured by Chevron Chemical Co. and sold under the tradename Ortho X-77; paraffin based petroleum oil, polyoxyethylated polyol fatty acids and polyol fatty esters, manufactured by Helena Chemical Co. and sold under the tradename Agridex; DASH, a tradename of a proprietary blend of surfactants manufactured by BASF Corporation; crop oil concentrate; and silicone based additives.

In addition to the foregoing, inert adjuvants can also be incorporated into the compositions of this invention to provide a more satisfactory formulation. Such inert adjuvants include spreaders, emulsifiers, dispersing agents, foaming adjuvants, foam suppressants, penetrants and correctives.

The term herbicide is used herein to denote a compound which controls or modifies the growth of plants. The term herbicidally effective amount is used to indicate the quantity of such compound or combination of such compound which is capable of producing a controlling or modifying effect. Controlling or modifying effects include all deviations from natural development, for example: killing, retardation, leaf burn, dwarfing and the like. The term plants is used to include all postemergent vegetation, ranging from seedlings to established vegetation.

The term nitrogen fertilizer is used herein to denote a primary nutrient that is required by all plants in considerable quantities for plant growth. Certain fertilizers have been used by applicators as carriers for pesticides. This type of application method allows the grower to apply the nitrogen and herbicide at the same time in one operation. The benefits of this system are reduced time and labor needs.

Application rates will depend upon the weeds to be controlled and the degree of control desired. In general, the

compositions of this invention are most efficiently employed at a rate of 0.001 to 20 pounds per acre (0.001 to 22.4 kilograms per hectare) of the active ingredients, preferably 0.01 to 15 pounds per acre (0.01 to 16.8 kilograms per hectare).

Usually, the nitrogen source and adjuvants are added independently to the spray mixture as a percent of the total spray volume or as gallons of product per acre. A preferred application range is 0.001 to 200 gallons of product per acre, more preferably about 0.01 to 5.0 gallons of product per acre, and most preferably about 0.1 to 2 gallons of product per acre for UAN and adjuvants.

An important factor influencing the usefulness of a given herbicide is its selectivity towards crops. In some cases a beneficial crop is susceptible to the effects of the herbicide. In addition, certain herbicidal compounds are phytotoxic to some weed species but not to others. To be effective, an herbicide must cause minimal damage to the beneficial crop while maximizing damage to weed species which infest the locus of the crop.

To preserve the beneficial aspects of herbicide use and to minimize crop damage, many herbicide antidotes or safeners have been prepared. Therefore, another embodiment of this invention includes the use of antidotes in the herbicidal composition. See U.S. Patent Nos. 4,021,224 (Pallos et al., May 3, 1977) and specifically 4,938,796 (Buren et al., July 3, 1990) for antidoted composition comprising substituted acylated 1,3-dicarbonyl compounds. This reference is hereby incorporated by reference in its entirety.

Representative antidotes for use with herbicides which are contemplated as being suitable for this invention include, e.g., compounds selected from the group consisting of amides of haloalkanoic acids (U.S. Patents 4,256,481; 4,294,764; 4,021,224); aromatic oxime derivatives (U.S. Patent 4,070,389); thiazole carboxylic acids and derivatives thereof (4,199,506); aryl cyclopropane carbonitrile derivatives (U.S. Patent

4,859,232); and 1,8-naphthalic anhydride. Specific compounds include 2,2-dimethyl-N-dichloroacetylthiazolidine; N,N-diallyl dichloroacetamide (R25788); 2,2-dimethyl-3-dichloroacetyl oxazolidine; 2,2,5-trimethyl-N-dichloroacetyl oxazolidine (R29148); 2,2-spirocyclohexyl-N-dichloroacetyl oxazolidine (AD-67); 2,2-di-chloro-1-(1,2,3,4-tetrahydro-1-methyl-2-isoquinolyl) (ethanone); 2,2-dimethyl-5-n-propyl-N-dichloroacetyl oxazolidine; α-[(1,3-dioxypyran-2-yl-methoxy)-imino] benzeneacetonitrile; naphthalic anhydride; 2-chloro-4-(trifluoromethyl) phenylmethyl ester (flurazole); and the like.

The amount of a given antidote to be utilized in combination with the mixture in the composition of this invention and the manner of its utilization will vary according to the particular antidote to be employed, the crop which is to be protected, the amount or rate of herbicide to be applied, and the soil and climatic conditions of the agricultural environment in which the mixture is to be applied. The selection of a specific antidote for use in the compositions, the manner in which it is to be applied (e.g., tank mix, in furrow application, seed treatment, etc.), the determination of activity which is nonphytotoxic but antidotally effective, and the amount necessary to provide this result, can be readily performed utilizing the test procedures in the cited patents such as U.S. Patent No. 4,938,796, in accordance with common practice in the art.

Herbicidal Evaluations

Herbicidal evaluations of mixtures of substituted cyclohexanediones and UAN with various surfactants.

EXAMPLE I

This example demonstrates the response of 2-(2-chloro-3-ethoxy-4-ethylsulfonylbenzoyl)-5-methyl-1,3-cyclohexanedione, urea ammonium nitrate (UAN) and surfactants in combined postemergence application to a variety of weeds.

The weed species were as follows:

Abbreviation	Common Name	Scientific Name
SETFA	giant foxtail	Seteria faberii
IPOSS	morningglory	Ipomoea sp.
ABUTH	velvetleaf	Abutilon theophrasti
SETSS	foxtail sp.	Setaria sp.
ECHCG	barnyardgrass	Echinochloa crus-galli
AMARE	redroot pigweed	Amaranthus retroflexus
XANSS	cocklebur sp.	Xanthium sp.

The crop species were as follows:

CN	corn	Zea maize (L.)

The experiment was a randomized complete block design with three replicates. Plots were 6' x 14'. Treatments were applied at the 7-8 leaf stage of corn by tank-mix. At dates approximately 18 days and 28 days after treatment, the degree of injury or control of the weeds was determined by visual comparison of untreated plants treated at the same time. The injury rating, on a scale of 0 to 100%, was recorded for each species as percent control, with 0% representing no injury and 100% representing complete kill. The results of these tests are contained in the following Tables I and II. Additionally, an untreated control in which the plot was untreated with any components of the claimed composition resulted in 0% weed control.

TABLE I

Percent corn phytoxicity and weed control at 18 days after application with compositions including 2-(2-chloro-3-ethoxy-4-ethylsulfonylbenzoyl)-5-methyl-1,3-cyclohexanedione as an herbicide

Treatment	Rate[1] lb/A	%V/V	CN	IPOSS	ABUTH	SETFA	ECHCG	AMARE	XANSS	SETSS
ORTHO-X-77	0.0625	0.5	0	0	45	55	65	62	64	48
	0.125	0.5	0	0	55	68	94	64	47	67
	0.250	0.5	0	33	91	88	95	83	58	89
AGRIDEX	0.0625	1.0	0	0	40	40	92	63	17	43
	0.125	1.0	0	10	55	45	75	42	33	53
	0.250	1.0	0	27	84	73	98	68	67	78
DASH	0.0625	1.0	0	13	47	57	91	78	0	52
	0.125	1.0	0	22	80	89	99	80	32	78
	0.250	1.0	0	28	99	97	98	78	55	95
ORTHO-X-77 +UAN	0.0625	0.5+4.0	0	38	98	80	97	73	37	80
	0.125	0.5+4.0	0	43	95	82	94	73	38	82
	0.250	0.5+4.0	0	70	100	99	100	99	95	99
AGRIDEX +UAN	0.0625	1.0+4.0	0	47	99	97	99	98	33	92
	0.125	1.0+4.0	0	42	100	98	99	80	58	99
	0.250	1.0+4.0	0	68	100	100	100	100	95	100
DASH +UAN	0.0625	1.0+4.0	0	53	100	100	100	80	15	100
	0.125	1.0+4.0	0	68	99	100	100	100	97	100
	0.250	1.0+4.0	0	80	100	100	100	98	95	100
CONTROL	0.0625	---	0	0	27	0	0	0	0	0
	0.125	---	0	0	22	0	32	13	0	0
	0.250	---	0	12	53	27	40	65	12	45

[1] 2-(2-chloro-3-ethoxy-4-ethylsulfonylbenzoyl)-5-methyl-1,3-cyclohexanedione

TABLE II

Percent corn phytoxicity and weed control at 4 weeks after application with 2-(2-chloro-3-ethoxy-4-ethylsulfonylbenzoyl)-5-methyl-1,3-cyclohexanedione as an herbicide

Treatment	Rate[1] lb/A	%V/V	CN	IPOSS	ABUTH	SETFA	ECHCG	AMARE	XANSS	SETSS
ORTHO-	0.0625	0.5	0	0	53	48	65	57	4	58
X-77	0.125	0.5	0	15	57	63	88	53	15	63
	0.250	0.5	0	0	82	69	100	78	48	88
AGRIDEX	0.0625	1.0	0	0	28	28	72	38	22	32
	0.125	1.0	0	0	43	37	49	32	0	43
	0.250	1.0	0	15	60	58	95	68	58	76
DASH	0.0625	1.0	0	0	35	48	88	73	23	53
	0.125	1.0	0	0	78	81	100	78	40	78
	0.250	1.0	0	15	94	99	100	87	52	100
ORTHO-	0.0625	0.5+4.0	0	0	80	63	82	58	55	65
X-77	0.125	0.5+4.0	0	28	90	73	97	43	72	72
+UAN	0.250	0.5+4.0	0	48	100	99	100	100	98	99
AGRIDEX	0.0625	1.0+4.0	0	13	99	90	91	90	0	89
+UAN	0.125	1.0+4.0	0	0	100	95	98	78	45	92
	0.250	1.0+4.0	0	57	100	100	100	100	99	100
DASH	0.0625	1.0+4.0	0	33	100	100	100	77	23	98
+UAN	0.125	1.0+4.0	0	55	100	100	100	100	67	100
	0.250	1.0+4.0	0	72	100	100	100	92	100	100
CONTROL	0.0625	---	0	0	0	0	0	0	0	0
	0.125	---	0	0	32	22	12	0	17	27
	0.250	---	0	0	42	5	23	33	38	22

[1] 2-(2-chloro-3-ethoxy-4-ethylsulfonylbenzoyl)-5-methyl-1,3-cyclohexanedione

As shown by the data in Tables I and II, addition of the nonionic surfactants and UAN did not increase corn injury at the higher rates of cyclohexanedione application. The analysis reveals that the combination of cyclohexanedione, UAN and surfactant has a different degree of effectiveness on various weed species, but it is clear that the addition of UAN to the composition increases weed control across all tested weed species with the exception of ECHCG. The composition of this invention was particularly effective at lower application rates of 0.063 and 0.125 lbs/acre cyclohexanedione.

Formulations

The compounds and compositions of this invention can be formulated in the same manner in which herbicides are generally formulated. The object of the formulation is to apply the compounds and compositions to the locus where control is desired by conventional method. The locus may include soil, seeds, seedlings, crop, crop seeds and vegetation.

Useful formulations of the compounds of this invention can be prepared in conventional ways. They include dusts, granules, microcapsules, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates and the like. Many of these may be applied directly to the locus. Sprayable formulations can be extended in suitable media and used at spray volumes of from a few liters to several hundred liters per hectare. High strength compositions are primarily used as intermediates for further formulation. The formulations, broadly, contain about 0.1% to 99% by weight of active herbicide and antidote ingredient(s) and optionally at least one of (a) about 0.1% to 20% surfactant(s) and (b) about 1% to 99.9% solid or liquid inert diluent(s). More specifically, they can contain these ingredients in the following approximate proportions.

TABLE VII

	Active Herb. & Ant. Ingredients	Weight Percent * Diluent(s)	Surfactant(s)
Wettable Powders	20-90	0-74	1-10
Oil Suspensions	3-50	40-95	0-15
Emulsions, Solutions (Including Emulsifiable Concentrates)			
Aqueous Suspension	10-50	40-84	1-20
Dusts	1-25	70-99	1-20
Granules and Pellets	0.1-95	5-99.9	0-15
Compositions	90-99	0-10	0-2

* Active ingredient plus at least one of a Surfactant or a Diluent equals 100 weight percent.

Lower or higher levels of active ingredient can be present depending on the intended use and the physical properties of the compound. Higher ratios of surfactant to active ingredient are sometimes desirable, and are achieved by incorporation into the formulation or by tank mixing.

Dusts are free-flowing powder compositions containing the formulant impregnated on a particulate carrier. The particle size of the carriers is usually in the approximate range of 30 to 50 microns. Examples of suitable carriers are talc, bentonite, diatomaceous earth, and pyrophyllite. The composition generally contains up to 50% of formulant. Anti-caking and anti-static agents may also be added. Dusts may be applied by spraying from boom sprayers, hand sprayers or airplanes.

Wettable powders are finely divided compositions comprising a particular carrier impregnated with the formulant and additionally containing one or more surface active agents. The surface active agent promotes rapid dispersion of the powder in an aqueous medium to form stable, sprayable suspensions. A wide variety of surface active agents can be used, for example, long chain fatty alcohols and alkali metal salts of sulfated fatty alcohols; salts of sulfonic acid; esters of long chain fatty acids; and polyhydric alcohols, in which the alcohol groups are free, omega-substituted polyethylene glycols of relatively long chain length. A list of surface active agents suitable for use in agriculture formulations can be found in Wade Van Valkenburg, Pesticide Formulations (New York: Marcel Dekker, Inc., 1973), pages 79-84.

Granules comprise the formulant impregnated on a particulate inert carrier having a particle size of about 1 to 2 millimeters (mm) in diameter. The granules can be made by spraying a solution of the formulant in a volatile solvent onto the granular carrier. Examples of suitable carriers for the preparation of granules include clay, vermiculate sawdust, and granular carbon.

Microcapsules and other slow release formulations are advantageous as formulations to deliver and distribute the active ingredients. Microcapsules consist of fully enclosed droplets or granules containing the active materials in which the enclosing material is an inert porous membrane, arranged to allow escape of the enclosed materials to the surrounding medium at controlled rates over a specified period of time. Encapsulated droplets are typically about 1 to 50 microns in diameter. The enclosed liquid typically constitutes about 50 to 95% of the weight of the entire capsule, and may contain an amount of solvent in addition to the active materials. Encapsulated granules are characterized by porous membranes sealing the openings of the granule carrier pores, trapping the liquid containing the active components inside for controlled release. A typical

granule size ranges from 1 millimeter to 1 centimeter in diameter. In agricultural usage, the granule size is generally about 1 to 2 millimeters in diameter. Granules formed by extrusion, agglomeration or prilling are useful in the present invention as well as materials in their naturally occurring form. Examples of such carriers are vermiculite, starch sintered clay granules, kaolin, attapulgite clay, sawdust and granular carbon. Useful encapsulating materials include natural and synthetic rubbers, cellulosic materials, styrene-butadiene copolymers, polyacrylonitriles, polyacrylates, polyesters, polyamides, polyureas, polyurethanes and starch xanthates.

Emulsifiable concentrates consist of an oil solution of the formulant plus and emulsifying agent. Prior to use, the concentrate is diluted with water to form a suspended emulsion of oil droplets. The emulsifiers used are usually a mixture of anionic and nonionic surfactants. Other additives, such as suspending agents and thickeners, may be included in the emulsifiable concentrate.

When the formulant is an antidote and herbicide composition, the proportion of antidote compound to herbicide compound generally ranges from approximately 0.001 to 30 parts by weight of the antidote compound per weight of the herbicide compound.

Formulations generally contain several additives in addition to the formulant and carrier or agent. Among these are inert ingredients, diluent carriers, organic solvents, water, oil and water, water in oil emulsions, carriers of dust and granules, and surface active wetting, dispersing and emulsifying agents. Fertilizers useful in combination with the active ingredients of this invention include, for example: potash, urea, superphosphate, and ammonium sulfate.

The composition of the invention may comprise one or more compounds which possess biological activity.

Examples of useful complementary herbicides include:

1. Anilides

Alachlor - 2-chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide

Metolachlor - 2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide

Propanil - N-(3,4-dichlorophenyl)propionanilide

Propachlor - 2-chloro-N-isopropylacetanilide

Butachlor - 2-chloro-2',6'-diethyl-N-(butoxymethyl) acetanilide

Acetochlor - 2-chloro-N-(ethoxymethyl)-6'-ethyl-O-acetotoluidide

Metazachlor-2-chloro-2',6'-dimethyl-N-(1-pyrazol-1-yl methyl) acetanilide

2. Triazines

Atrazine - 2-chloro-4-(ethylamino)-6-isopropylamino)-s-triazine

Cyanazine - 2-chloro-4-(1-cyano-1-methylethylamino)-6-ethylamino-s-triazine

Metribuzin - 4-amino-6 -tert-butyl-3-(methylthio)-1,2,4-triazin-5(4H)-one

Simazine - 2-chloro-4,6-bis (ethylamino)-1,3,5-triazine

3. Thiocarbamates

Molinate - S-ethyl hexahydro-1H-azepine-1-carbothioate

Butylate - S-ethyl diisobutylthiocarbamate

EPTC - ethyl dipropulthiolcarbamate

Triallate - 2,3,3-trichloroallyl-diisopropylthiolcarbamate

Diallate - cis-1-trans-2,3-dichloroallyl-diisopropylthiol-carbamate

Vernolate - S-propyl dipropylthiolcarbamate

4. Ureas

Monuron - 3-(p-chlorophenyl)-1,1-dimethylurea

Linuron - 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea

1-(1-cyclohexen-1-yl)-3-(2-fluoro phenyl)-1-methyl urea

3-[4-(4-halophenoxy)phenyl]-1,1-dialkylur as

5. Toluidines

Trifluralin - α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine

Pendimethalin - N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitro-benzeneamine

6. Hormones

2,4-D - (2,4-dichlorophnoexy) acetic acid

MCPA - (2-methyl-4-chlorophenoxy) acetic acid

Dichlorprop - 2,4,5-trichlorophenoxy acetic acid

MCPB - 4-(4-chloro-2-methyl phenoxy)butynic acid

2,4,5-T - 2,4,5-trichlorophenoxy acetic acid

Mecoprop - 2-(4-chloro-2-methyl phenoxy) propionic acid and their derivatives

7. Diazines

Bentazon - 3-isopropyl-1H-2,3,1-benzothiadiazin-4(3H)-one 2,2-dioxide

Oxadiazon - 2-tert-butyl-4-(2,4-dichloro-5-isopropoxy-phenyl)-Δ^2-1,3,4-oxadiazolin-5-one

8. Diphenyl ethers

Acifluorfen - sodium 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoate

Fluazifop-butyl -(±)-butyl 2-[4[(5-(trifluoromethyl)-2-pyridinyl)oxy]phenoxy]propanoate

Chlomethoxynil - 2,4-dichlorophenyl 3-methoxy-4-nitro-phenyl ether

Fomesafen - 5-[2-chloro-4-(trifluoromethyl)phenoxy]-N-(methyl-sulfonyl)-2-nitrobenzamide

Sethoxydim - 2[1-(ethoxyimino)butyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1 -one

9. Imidazolinones

Imazaquin - 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinolin carboxylic acid

Imazethapur (±)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl0-5-oxo-1H-imidazol-2-yl]-5-et hyl-3-pyridinecarboxylic acid

10. Sulfonyl ureas

Bensulfuron methyl - methyl 2-[[[[[(4,6-dimethoxypyrimidin-2-yl)amino]carbonyl]amino]sulfonyl]methyl]benzoate

Chlorimuron ethyl - ethyl 2-(((((4-chloro-6-methoxypyrimidin-2-yl)amino)carbonyl)amino)sulfonyl) benzoate

Chlorosulfuron - 2-chloro-N-(4-methoxy-6-methyl-1,3,5-triazine-2-yl)-amino carbonyl) benzene sulphoamide

Nicosulfuron - 3-pyridimecarboxamide,2-[([4,6-dimethoxypyrimidin 2-yl]amino-carbonyl)aminosulfonyl]-N,N-dimethyl

Primisulfuron - 3-[4,6-Bis-(difluoromethoxy)-pyrimidin-2-yl]-1-(2-methoxycarbonylphenylsulfonyl)urea

Flumetsulam (proposed) - N-[2,6-difluorophenyl]-5-methyl(1,2,4) triazolo-[1,5a]-pyrimidine-2-sulfonamide

11. Dinitrophenols

DNOC - 2 methyl-4,6-dinitrophenol

Dinoterb - 2-t-hidyl-4,6-dinitrophenol

12. Miscellaneous Compounds

Dimethazone - 2-(2-chlorophenyl)methyl-4,4-dimethyl-3-isoxazolidinone

Norflurazon - 4-chloro-5-(methylamino)-2-α,α,α-trifluoro-m-tolyl)-3-(2H)-pyridazinone

Dalapon - 2,2-dichloropropionic acid

Glyphosate - isopropyl amine salt of N-(phosphonomethyl) glycine

Fenoxaprop-ethyl - (+)-ethyl-2,4-((6-chloro-2-benzoxazoly loxy)phenoxy)propanoate

Organoarsenical herbicides such as MSMA - monosodium methanearsonate

Paraquat - 1,1'-dimethyl-4,4'-dipyridylium ion

Pyridate O - (6-chloro-3- 3 phenyl-4-pyridazinyl)S-octyl carbonothioate

13. Benzoic acids

2,3,6-TBA - 2,3,6-trichlorobenzoic acid

Dicamba - 3,6-dichloro-2-methoxy-benzoic acid

Chloramben - 3-amino-2,5-dichloro benzoic acid

Alternatively, the compounds and compositions of this invention can be applied to a crop by addition to irrigation water supplied to the field to be treated. This method of application permits the penetration of the compositions into the soil as the water is absorbed therein.

As another alternative, the formulation can be applied to the soil in the form of a solution in a suitable solvent. Solvents frequently used in these formulations include kerosene, fuel oil, xylene, petroleum fractions with boiling ranges above xylene and aromatic petroleum fractions rich in methylated naphthalenes. Liquid solutions, like dusts, may be applied by spraying from boom and hand sprayers or airplanes.

Herbicide formulations of the types described above are exemplified in several illustrative examples below.

Example I

Dusts: The following substances are used to formulate a 5% dust:

5 parts of active substance
95 parts of talc

Example II

Granulate: The following substances are used to formulate a 5% granulate:

5 parts of active substance
0.25 part of epichlorohydrin
0.25 part of cetyl polyglycol ether
3.25 parts of polyethylene glycol
91 parts of kaolin (particle size 0.3-0.8 mm).

The active substance is mixed with epichlorohydrin and the mixture is dissolved in 6 parts of acetone. Then polyethylene glycol and cetyl polyglycol ether are added. The resultant

solution is sprayed on kaolin and the acetone is evaporated *in vacuo*.

Example III

Wettable powders: The following constituents are used to formulate (a) a 70%, (b) a 25%, and (c) a 25% wettable powder:

(a)
70 parts of active substance
5 parts of sodium dibutylnaphthylsulfonate
3 parts of naphthalenesulfonic acid/phenolsulfonic acid/formaldehyde condensate (3:2:1)
10 parts of kaolin
12 parts of Champagne chalk

(b)
25 parts of active substance
4.5 parts of calcium ligninsulfate
1.9 parts of Champagne chalk/hydroxyethyl cellulose mixture (1:1)
1.5 parts of sodium dibutylnaphthalenesulfonate
19.5 parts of silicic acid
19.5 parts of Champagne chalk

(c)
25 parts of active substance
2.5 parts of isoctylphenoxy-polyethylene-ethanol
1.7 parts of a Champagne chalk/hydroxyethyl cellulose mixture (1:1)
8.3 parts of sodium aluminum silicate
16.5 parts of kieselguhr
46 parts of kaolin

The active substances are intimately mixed in suitable mixers with the additives and ground in appropriate mills and rollers. Wettable powders of excellent wettability and suspension power are obtained. These wettable powders can be diluted with water to give suspensions of the desired concentration and can be used in particular for treating parts of plants.

Example IV

Emulsifiable concentrate: The following substanc s are used to formulate a 25% emulsifiable concentrate:

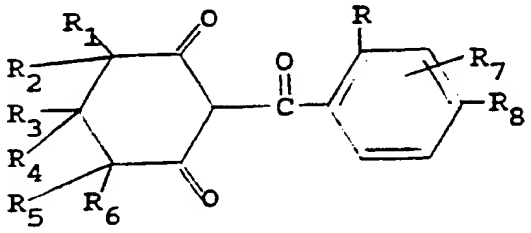
25 parts of active substance
2.5 parts of epoxidized vegetable oil
10 parts of an alkylarylsulfonate/fatty alcohol polyglycol ether mixture
5 parts of dimethylformamide
57.5 parts of xylene.

By diluting such a concentrate with water, it is possible to prepare emulsions of the desired concentrations, which are especially suitable for leaf application.

What is claimed is:

1. A herbicidal composition comprising

(a) an herbicidally effective amount of a substituted cyclohexandione of the formula



in which

R is halogen; C_1-C_2 alkyl, preferably methyl; C_1-C_2 alkoxy, preferably methoxy; nitro; cyano; C_1-C_2 haloalkyl, preferably trifluoromethyl; or R^aSO_n- wherein n is 0 or 2, preferably 2 and R^a is C_1-C_2 alkyl, preferably methyl. Preferably, R is chlorine, bromine, C_1-C_2 alkyl, C_1-C_2 alkoxy, cyano, nitro, C_1-C_2 alkylthio or C_1-C_2 alkylsulfonyl; more preferably chlorine, nitro, methyl, trifluoromethyl or methylsulfonyl;

R_1, R_2, R_3, R_4, R_5 and R_6 are independently hydrogen; C_1-C_4 alkyl, preferably C_1-C_2 alkyl, more preferably methyl or hydrogen;

R_7 and R_8 are independently (1) hydrogen; (2) halogen, preferably chlorine, fluorine or bromine; (3) C_1-C_4 alkyl, preferably methyl; (4) C_1-C_4 alkoxy, preferably methoxy or ethoxy; (5) trifluoromethoxy; (6) cyano; (7) nitro; (8) C_1-C_4 haloalkyl, more preferably trifluoromethyl; (9) R^bSO_n- wherein n is the integer 0, 1 or 2, preferably 0 or 2; and R^b is (a) C_1-C_4 alkyl, preferably methyl; or (b) C_1-C_4 alkyl substituted with halogen, preferably chloromethyl, or trifluoromethyl; (10) $-NR^cR^d$ wherein R^c and R^d are independently hydrogen or C_1-C_4 alkyl; (11) $R^eC(O)$- wherein R^e is C_1-C_4 alkyl or C_1-C_4 alkoxy; (12) $-SO_2NR^cR^d$ wherein R^c and R^d are as defined; (13) $-N(R^c)C(O)R^d$ wherein R^c and R^d are as defined; and (14) $-CH_2CH_2OCH_3$ or $-CH_2CH_2OC_2H_5$;

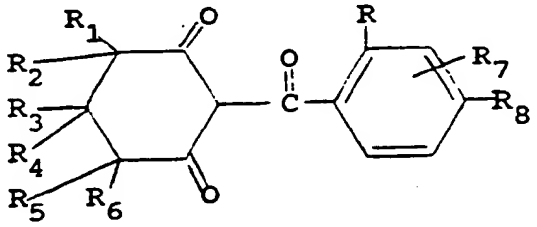
(b) at least one nitrogen containing fertilizer that is present in an amount that increases the herbicidal activity of said substituted cyclohexanedione; and

(c) one or more adjuvants.

2. A composition according to Claim 1 further comprising a substantially non-phytotoxic, antidotally effective amount of a cyclohexanedione herbicide antidote.

3. A herbicidal composition comprising

(a) an herbicidally effective amount of a substituted cyclohexandione of the formula



in which

R is halogen;

R_1, R_2, R_3, R_5, and R_6 are each hydrogen or C_1-C_2 alkyl;

R_4 is hydrogen or C_1-C_4 alkyl

R_7 is hydrogen, C_1-C_3 alkoxy, $-CH_2CH_2OCH_3-$, $-CH_2CH_2OC_2H_5$, C_1-C_4 thioalkyl; and

R_8 is halogen, trifluoromethyl or R^bSO_n wherein R^b is C_1-C_4 alkyl and n is 0 or 2;

(b) Urea ammonium nitrate wherein the % N is about between 28-33%; and

(c) one or more surfactants.

4. A composition according to Claim 3 further comprising a substantially non-phytotoxic antidotally effective amount of a cyclohexanedione herbicide antidote.

5. A composition according to Claim 4 in which the antidote is an amide of a haloalkanoic acid, an aromatic oxime derivative, a triazole carboxylic acid or derivative thereof, or 1,8-naphthalic anhydride.

6. A composition according to Claim 5 wherein said amide of a haloalkanoic acid is an amide wherein the nitrogen atom thereof is in an oxazolidine.

7. A composition according to Claim 5 wherein said amide of haloalkanoic acid is dichloroacetic acid.

8. A composition according to Claim 3 wherein R is Cl.

9. A composition according to Claim 8 wherein R_4 is hydrogen or methyl.

10. A composition according to Claim 9 wherein R_7 is C_1-C_3 alkoxy.

11. A composition according to Claim 10 wherein R_8 is R^bSO_n wherein R^b is C_1-C_4 alkyl and n is 2.

12. A composition according to Claim 3 wherein said substituted cyclohexanedione is 2-(2-chloro-3-ethoxy-4-ethyl-sulfonyl benzoyl)-1,3-cyclohexanedione.

13. A composition according to Claim 3 wherein said substituted cyclohexanedione is 2-(2-chloro-3-ethoxy-4-ethyl-sulfonyl benzoyl)-5-methyl-1,3-cyclohexanedione.

14. A composition according to Claim 3 wherein said surfactant is a nonionic surfactant.

15. A composition according to Claim 3 wherein said surfactant is an oil selected from vegetable or petroleum.

16. A composition according to Claim 3 comprising a second pesticide.

17. An herbicidal composition comprising an herbicidally effective amount of 2-(2-chloro-3-ethoxy-4-ethyl sulfonyl benzoyl)-5-methyl-1,3-cyclohexanedione; urea ammonium nitrate and one or more adjuvants.

18. A composition according to Claim 17 further comprising a substantially non-phytotoxic antidotally effective amount of a cyclohexanedione herbicide antidote.

19. A composition according to Claim 17 further comprising a second pesticide.

20. A method of controlling undesirable vegetation in the presence of a crop comprising the post-emergence application to the locus of said vegetation or said crop a herbicidal composition according to Claim 3.

21. A method according to Claim 20 in which the substituted cyclohexanedione is 2-(2-chloro-3-ethoxy-4-ethyl-sulfonyl benzoyl)-1,3 cyclohexanedione.

22. A method according to Claim 20 in which the substituted cyclohexanedione is 2-(2-chloro-3-ethoxy-4-ethyl-sulfonyl benzoyl)-5-methyl-1,3 cyclohexanedione.

23. A method according to Claim 20 further comprising applying to said locus a substantially non-phytotoxic antidotally effective amount of a cyclohexanedione herbicide antidote.

24. A method according to Claim 20 in which the crop is corn.

25. An herbicidal composition comprising:
(a) an herbicidally effective amount of a substituted 2-benzoyl-1,3-cyclohexanedione; and
(b) at least one nitrogen containing fertilizer that is present in an amount that increases the herbicidal activity of said substituted 2-benzoyl-1,3-cyclohexanedione.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/03551

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 A01N35/06; A01N41/10; //(A01N35/06,47:28, 59:00) (A01N41/10,47:28, 59:00)

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	A01N

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	EP,A,0 137 963 (STAUFFER CHEMICAL COMPANY) 24 April 1985 & US,A,4 780 127 25 October 1988 cited in the application	
A	EP,A,0 350 079 (STAUFFER CHEMICAL COMPANY) 10 January 1990 & US,A,4 759 794 26 July 1988 cited in the application	
A	EP,A,0 298 680 (ICI AMERICAS INC.) 11 January 1989 & US,A,4 938 796 3 July 1990 cited in the application	

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
14 SEPTEMBER 1992	25.09.92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	DONOVAN T.M.

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9203551 SA 60535

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 14/09/92
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		CA-A-	1258869	29-08-89
		DE-A-	3474297	03-11-88
		JP-B-	1030818	22-06-89
		JP-C-	1548106	09-03-90
		JP-A-	60087238	16-05-85
		US-A-	5006162	09-04-91
		US-A-	4780127	25-10-88
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		US-A-	4853028	01-08-89
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The members are as contained in the European Patent Office EDP file on
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		JP-A-	1117803	10-05-89